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## RAREFACTION SHOCK POSSIBILITY IN A VAN DER WAALS-MAXWELL FLUID

by

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October 1968

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REPORT NO. 1421

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G. D. Kahl and D. C. Mylin

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REPORT NO. 1421

GDKahl/DCMylin/so  
Aberdeen Proving Ground, Md.  
October 1968

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ABSTRACT

The rarefaction shock is found to be impossible practically in an equilibrium Van der Waals-Maxwell fluid, in and across all phase regions. The existence of this type shock depends explicitly on the constant-volume specific heat, as well as the pressure equation of state. The form of specific heat assumed here includes contributions from translation, rotation, and vibration energies of the molecule; Einstein functions are used to represent the latter. In particular, the vaporizing expansion wave in the saturated liquid phase cannot be discontinuous. Metastable states of supersaturation are not considered. Despite the results for this theoretical model, the necessary conditions for the rarefaction shock are found to be satisfied, in principle, for a small region near the critical point of a real two-phase fluid (steam).

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## I. INTRODUCTION

In most fluids, including the ideal gas, an initial compressive disturbance steepens with time into a compressive shock discontinuity, while an expansive disturbance flattens out, never producing a discontinuity. This type of response depends on the equation of state for the fluid. In principle, the possibility of contrary responses to initial disturbances exists in fluids obeying certain state equations. For example, Paxton<sup>1</sup> discusses the rarefaction shock possibility in a plasma carrying a large electrical current. And Zeldovich and Raizer<sup>2</sup> cite a possible rarefaction discontinuity in the gaseous phase of a Van der Waals-Maxwell fluid near its critical point; their treatment of this problem is a reproduction of one given earlier by Zeldovich<sup>3</sup> in 1947.

A detailed analysis of the shock discontinuity for arbitrary state equations was made in 1942 by Bethe<sup>4</sup> in a report of initially limited distribution. And it is shown in [4] that the probability of satisfying a necessary condition for the non-MHD rarefaction shock in the gaseous phase of a substance is practically non-existent, including the specific fluid treated in [2] and [3]. The equilibrium coexistence phase of both liquid and vapor was not considered.

In this paper, the two-phase region of the Van der Waals-Maxwell fluid is examined. Motivation for this investigation is provided by observations on exploding wires. The early electrical resistance of many exploding wires fits a model which assumes a vaporizing expansion wave proceeding radially inward from the cylindrical surface, shrinking the conducting cross section of the intact molten interior<sup>5,6</sup>. The existence of such a wave can be predicted from a two-phase fluid model; and the Van der Waals-Maxwell fluid yields wave velocities which are in fair agreement with experiment<sup>7</sup>. It is of interest to know whether this model will predict a steepening of this expansion wave into a finite rarefaction shock. Although the discontinuous part of the

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\*References are found on page 29.

expansion is not an absolute necessity for the experimental interpretation, it would assist in offering a simple and conceptually plausible explanation for the resistance behavior.

This treatment is limited to thermodynamic equilibrium, thereby excluding metastable conditions such as superheating or supercooling of one of the phases. Although ever mounting evidence shows the Van der Waals-Maxwell model is not an accurate description in the critical region of a fluid, it is still valuable for its simplicity, and as a standard of comparison for recent empirical proposals of state functions there. Recent computations of its coexistence properties have been made by Barieau<sup>8</sup>, and we adopt his notation for the scaled variables used here.

We find that the rarefaction shock possibility is even less likely in the two-phase region of this fluid than in the single phase, where it has already been shown to be practically impossible<sup>4</sup>. Then, despite the results with this model, we show by direct use of steam tables, as suggested by Novikov<sup>9</sup>, that the rarefaction shock possibility cannot be dismissed over a small part of the wet vapor state of steam near critical.

## II. DISCONTINUITY CONDITION

Let  $P$ ,  $V$ ,  $T$ , and  $S$  be pressure, specific volume, temperature, and specific entropy respectively. The change of entropy across a discontinuous transition of a system initially at the state  $(P_0, V_0, T_0, S_0)$  to the state  $(P, V, T, S)$  is given by

$$S - S_0 = - (V - V_0)^3 \left\{ \left( \frac{\partial^2 P}{\partial V^2} \right)_s \right\} / (12T_0) + \dots \quad (1)$$

This expression follows from several properties concerning the mechanical discontinuity relations which are proved by Courant and Friedrichs<sup>10</sup>. These properties are: a) the pressure function  $P = G(V)$  of the transition Hugoniot curve makes a second order contact with the pressure function  $P = g(V)$  of the adiabatic isentrope at the conditions

of the initial state; and b) the entropy change along the Hugoniot curve is third order in volume change from the initial state with  $\left(\frac{dS}{dV}\right)_0 = \left(\frac{d^2S}{dV^2}\right)_0 = 0$ , and  $\left(\frac{d^3S}{dV^3}\right)_0 = -\left(\frac{d^2G}{dV^2}\right)_0/(2T_0)$ . The first condition implies  $\left\{\left(\frac{\partial^2P}{\partial V^2}\right)_s\right\}_0 = \left(\frac{d^2G}{dV^2}\right)_0$ ; making a series expansion of  $(S-S_0)$  in terms of  $(V-V_0)$  then results in the first non-zero term shown in Eq. (1). Not all gas dynamic transitions possess the foregoing simple properties; a notable exception is the detonation wave. For our purpose, we have assumed that the fluid on both sides of the discontinuity obeys a unique state equation, so that the transition is neither exothermic nor endothermic; a discussion of the Hugoniot curves for these latter transitions is given by Hayes<sup>11</sup>.

The form of Eq. (1) shows that for the usual fluid where  $\left(\frac{\partial^2P}{\partial V^2}\right)_s$  is positive, the transition which increases the entropy forces  $V < V_0$ , as in a shock compression. Were  $\left(\frac{\partial^2P}{\partial V^2}\right)_s$  negative, however, then the condition for increased entropy would be  $V > V_0$ , corresponding to the rarefaction discontinuity. The possibility of the rarefaction shock process is seen to depend on  $\left(\frac{\partial^2P}{\partial V^2}\right)_s$  being negative. It is this quantity which we investigate for the Van der Waals-Maxwell fluid. The state functions  $P$ ,  $E$ , and  $S$  (where  $E$  is the internal energy) are expressed in terms of the independent variables  $V$  and  $T$ . We will use the differential operator

$$\left(\frac{\partial}{\partial V}\right)_s = \left(\frac{\partial T}{\partial V}\right)_s \left(\frac{\partial}{\partial T}\right)_v + \left(\frac{\partial}{\partial V}\right)_T \quad (2)$$

along with

$$TdS = dE + PdV \quad (3)$$

and the identity

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_v - P. \quad (4)$$

Both  $dE$  and  $dS$  are assumed exact differentials of  $V$  and  $T$  within given  $V, T$ , regions. The constant volume specific heat is  $C_v = \left(\frac{\partial E}{\partial T}\right)_v$ , and is assumed never negative. From Eq. (3) one finds  $\left(\frac{\partial E}{\partial V}\right)_s = -P$  directly, and application of operator (2) to  $E$ , and using (4) results in  $\left(\frac{\partial T}{\partial V}\right)_s = - (T/C_v) \left(\frac{\partial P}{\partial T}\right)_v$ ; again using Eq. (2) on  $P$  results in

$$\left(\frac{\partial P}{\partial V}\right)_s = - (T/C_v) \left(\frac{\partial P}{\partial T}\right)_v^2 + \left(\frac{\partial P}{\partial V}\right)_v. \quad (5)$$

With  $\underline{w}$  the adiabatic (and in this instance, isentropic) sound speed of the substance defined by  $w^2 = -V^2 \left(\frac{\partial P}{\partial V}\right)_s$ , the right side of Eq. (5) is seen to be  $-w^2/V^2$ . The sound speed is expected to be real and finite for a well-behaved fluid; since  $T$  and  $C_v$  are always positive, then  $\underline{w}$  will certainly be real if  $\left(\frac{\partial P}{\partial V}\right)_v \leq 0$ . This latter condition holds for most substances, including the Van der Waals-Maxwell fluid, which we now describe more completely.

### III. FLUID MODEL

The fluid may be either a liquid, vapor, or an equilibrium mixture of the two phases. For either of the single phases, the pressure is given by the Van der Waals function,

$$P_w(V, T) = \{\hat{R}T/(V-b)\} - a/V^2, \quad (T > 0, V > 0) \quad (6)$$

where  $\hat{R}$  is the gas constant for unit mass and  $\underline{a}$  and  $\underline{b}$  are constants typifying the substance. By choosing for unit mass the molar mass of the substance, one replaces  $\hat{R}$  with  $R$ , the universal gas constant. The  $(V, T)$  region where Eq. (6) applies is  $T > 0, V > 0$  except for the region of phase coexistence. The coexistence region is defined by  $T \leq T_c$  (where subscript  $c$  always denotes critical conditions) and  $V_3(T) \leq V \leq V_1(T)$ ,

with the loci  $V_3(T)$  and  $V_1(T)$  specified later. Within the region where Eq. (6) applies, a differentiation by  $T$  of Eq. (4) shows that  $C_v$  is independent of  $V$ . Outside coexistence, the fluid consists of a single phase, either liquid or vapor. For convenience we label the regions  $T \leq T_c$ ,  $b \leq V \leq V_3(T)$  as the liquid phase, and assert the vapor phase occurs in both  $T \geq T_c$ ,  $V \geq b$ , and in  $T \leq T_c$ ,  $V_1(T) \leq V$ .

The pressure in the equilibrium coexistence region is not  $P_W(V,T)$ , but is instead the vapor pressure function,  $P_A(T)$ , independent of  $V$ . This function is not defined explicitly; it must satisfy two conditions: a) the pressure across the coexistence boundary must be continuous, and b) the chemical potential, or Gibbs free energy function  $E - TS + PV$ , is constant for fixed  $T$  within coexistence, and is continuous across the boundaries. Both these conditions are satisfied by the Maxwell rule: for any  $T \leq T_c$ ,

$$\int_{V_3(T)}^{V_1(T)} P_W(V,T) dV = P_A(T) \{V_1(T) - V_3(T)\}, \quad (7)$$

with the subsidiary conditions  $P_W(V_1,T) = P_A(T) = P_W(V_3,T)$ . Eq. (7) and its subsidiary conditions fix  $P_A(T)$  and the  $V_3(T)$  and  $V_1(T)$  loci of the coexistence boundary. This Maxwell rule implicitly imposes the restriction for fixed  $T \leq T_c$  that  $C_v(T)(\text{liquid}) = C_v(T)(\text{vapor}) = C_v^0(T)$ . Although there is another suggested rule similar to Eq. (7) which relaxes this condition on the specific heats<sup>12</sup>, it is less convenient because it requires additional information about the difference of these specific heats. For simplicity, we confine present attention to the Van der Waals-Maxwell fluid with the coexisting phase region governed by Eq. (7).

The isotherm segments of  $P_A(T)$  are isobaric and extend from  $V_3(T)$ , the saturated liquid locus, to  $V_1(T)$ , the saturated vapor line. By replacing those portions of the mathematically defined but thermodynamically unacceptable isotherm segments of Eq. (6), with the acceptable isotherm segments of  $P_A(T)$  in the coexistence state, we have

removed any possibility that  $\left(\frac{\partial P}{\partial V}\right)_T$  might be positive for this fluid. This fact insures that the right hand side of Eq. (5) is negative in all regions of interest.

#### IV. SINGLE PHASE

We review briefly the conditions found in the single phase of this fluid. Allowing  $C_v$  to be a function of temperature alone, and successively applying operator (2) twice to Eq. (6), one finds

$$\left(\frac{\partial^2 P_w}{\partial V^2}\right)_s = \{RT/(V-b)^3\} \{\phi(T) - Y(V,T)\}, \quad (8)$$

with the dimensionless quantities

$$\phi(T) = (2 + R/C_v^0)(1 + R/C_v^0) - T(R/C_v^0)^3 \frac{d(C_v^0/R)}{dT}, \quad (9)$$

$$Y(V,T) = 6a(V-b)^3/(RTV^4). \quad (10)$$

We see two ways the right hand side of Eq. (8) can be negative.

First, if  $\phi(T) < 0$ , the right side is always negative because  $Y(V,T)$  is  $> 0$ , and  $V \geq b$ . For  $\phi(T) < 0$ , the rate of changes of  $C_v^0(T)$  with increasing  $T$  must be large. If  $\phi(T) < 0$ , then even the ideal gas might sustain a rarefaction shock. This fact may be seen by observing that the Van der Waals pressure function reduces to that of the ideal gas when both constants  $a$  and  $b$  of Eq. (6) are identically zero; the right side of Eq. (8) then becomes  $\phi(T)RT/V^3$ , with sign depending on  $\phi(T)$ . Thus, negative  $\phi(T)$  permits both the ideal gas and the single phases of the Van der Waals fluids to meet the necessary condition for the rarefaction shock. The probability of negative  $\phi(T)$  will be discussed in Section VII.

But there is a second way that the right side of Eq. (8) might be

negative. This condition occurs if

$$Y(V,T) > \phi(T) \quad (11)$$

for a particular  $(V,T)$  domain. The constants  $\underline{a}$  and  $\underline{b}$  can be expressed in terms of the critical values of  $P$ ,  $V$ , and  $T$ , as  $b = V_c/3$ ,  $a = (9/8)RT_cV_c$  and the relation  $P_cV_c = (3/8)RT_c$ . The function  $Y(V,T)$  has a maximum value with respect to  $V$  at  $V = 4b = (4/3)V_c$ ; meanwhile the permissible  $T$  values are bounded below by  $T(\min)$ , corresponding to values along the coexistence boundary, since Eq. (8) applies only to the single phase region. At  $V = (4/3)V_c$ ,  $T(\min) = .9834 T_c$ ; if  $C_v^0$  is constant with  $T$ , so  $\frac{d(C_v^0/R)}{dT} = 0$ , then inequality (11) can be satisfied for the dimensionless quantity  $(C_v^0/R) \geq 17.5$ . Very large values of  $(C_v^0/R)$  and/or  $\frac{d(C_v^0/R)}{dT}$  are needed to fulfill inequality (11), even when the specific volume lies in a small neighborhood slightly larger than critical volume. Again we defer discussion of  $C_v^0/R$  to a later section.

## V. COEXISTENCE STATE

### A. Justification of Model

This section deals only with the  $(V,T)$  region of coexisting phases of the fluid. However, some justification and caution is needed in applying continuum fluid mechanical concepts to this regime. The vapor pressure function,  $P_A(T)$ , used in the equilibrium two-phase region applies to a variety of combinations of coexisting liquid and vapor phases, requiring only that the phases have equal temperature and pressure. For example, the entire liquid phase could be located at one end of a container, with the vapor phase at the other; in this instance, a unique "sound" speed for the system would appear unjustified. The two-phase fluid mixture could approximate a continuous medium, providing each phase is dispersed within the other so that the mixture in a small volume appears homogenous on the length scale of that volume.

If, in addition, the dimensions of this volume are small enough that the mechanical relations may be reasonably approximated by differential equations, then continuum fluid mechanics can be used. We assume that these conditions apply in our further treatment of the coexistence state. In this connection, Cowperthwaite and Ahrens<sup>13</sup> have recently given a discussion of the thermodynamics of the adiabatic change of a system consisting of two phases at the same pressure. They find several ways such a change is also isentropic; one of these requires reversible heat exchange between the phases, with the mixture composition changing so that the phases remain in chemical equilibrium. Using the vapor pressure function,  $P_A(T)$ , defined by Eq. (7) as the pressure state equation for the coexistence region, insures equilibrium of both chemical potential and pressure; thus, infinitesimal adiabatic changes in this two-phase system will also be isentropic. The question of whether the finite adiabatic change of this type remains isentropic requires further investigation, and it is this problem that we are considering.

#### B. Specific Heat

By using  $P_A(T)$  for  $P$  in Eq. (4), integrating with respect to  $V$  from  $V_3(T)$  to  $V(T)$ , where  $\{V_3(T) \leq V \leq V_1(T)\}$ , and differentiating the result by  $T$ , one obtains the specific heat at constant volume for the coexistence region. It is  $C_{VA}(T)$ , given by

$$C_{VA}(V,T) = C_V^0(T) + A(T) + \{V-V_3(T)\} J(T), \quad (12)$$

where  $A(T) = V_3'(P_A - TP_A' + a/V_3^2)$  and  $J(T) = TP_A''$ , where the prime hereafter signifies ordinary temperature derivative, and  $C_V^0(T)$  is the constant volume specific heat outside coexistence. As expected,  $C_{VA}(V,T)$  is a linear function of  $V$ . A further useful relation can be obtained from Eq. (7), viz.,

$$TP_A' - P_A = a/(V_1V_3). \quad (13)$$

Eq. (13) results from differentiating Eq. (7) by  $T$ , applying the subsidiary conditions, multiplying the result by  $T$  and subtracting Eq. (7) from both sides. Computed values from Eq. (7), as well as limiting values as  $T \rightarrow T_c$  show that  $P_A'$ ,  $P_A''$ , and  $V_3'$  are all positive for  $T \leq T_c$ . It follows that  $J(T)$  is always positive in coexistence; since  $V_1 \geq V_3$ , using Eq. (13) in the definition of  $A(T)$  shows that  $A(T)$  is never negative here. Therefore,  $C_{VA}(V, T)$  is positive; since  $V_1 \geq V \geq V_3$  for any fixed  $T$ , one finds the inequality

$$0 < C_{VA}(V_3, T) \leq C_{VA}(V, T) \leq C_{VA}(V_1, T). \quad (14)$$

### C. Coexistence Isentropes

Since  $P_A(T)$  is independent of  $V$ ; using  $P_A(T)$  for  $P$  in Eq. (5) gives  $\left(\frac{\partial P_A}{\partial V}\right)_S = - (T/C_{VA})(P_A')^2$ . Using operator (2) on this latter expression, remembering that  $C_{VA}$  depends on both  $T$  and  $V$ , results in

$$\left(\frac{\partial^2 P_A}{\partial V^2}\right)_S = (T/C_{VA}^3)(P_A')^3 L(V, T), \quad (15)$$

where

$$L(V, T) = \{1 + 3J(T)/P_A'\} C_{VA} - T \left(\frac{\partial C_{VA}}{\partial T}\right)_V. \quad (16)$$

From Eq. (12) one finds

$$\left\{\left(\frac{\partial C_{VA}}{\partial T}\right)_V(V, T)\right\} = \left\{\left(\frac{\partial C_{VA}}{\partial T}\right)_V(V_3, T)\right\} + (V - V_3)J'(T) \quad (17)$$

where

$$\left\{\left(\frac{\partial C_{VA}}{\partial T}\right)_V(V_3, T)\right\} = C_V^0' + A' - JV_3'. \quad (18)$$

We show in the appendix that  $J'(T)$  is positive for  $T \leq T_c$ . With  $V \geq V_3(T)$  in coexistence, the following inequalities come from Eq. (17):

$$\left\{\left(\frac{\partial C_{VA}}{\partial T}\right)_V(V_3, T)\right\} \leq \left\{\left(\frac{\partial C_{VA}}{\partial T}\right)_V(V, T)\right\} \leq \left\{\left(\frac{\partial C_{VA}}{\partial T}\right)_V(V_1, T)\right\}. \quad (19)$$

Noting that  $P_A'$  and  $J(T)$  are positive quantities, one can make use of relations (14), (19), (16) and (15) to obtain the further inequality

$$L(V_1, T) \leq L(V, T) \leq L(V_3, T), \quad (20)$$

and consequently

$$\left\{ \left( \frac{\partial^2 P_A}{\partial V^2} \right)_s (V_1, T) \right\} \leq \left\{ \left( \frac{\partial^2 P_A}{\partial V^2} \right)_s (V, T) \right\} \leq \left\{ \left( \frac{\partial^2 P_A}{\partial V^2} \right)_s (V_3, T) \right\}. \quad (21)$$

Inequality (21) shows that the size of the second volume derivatives of the isentropes in coexistence is bounded between the value on the saturated liquid and vapor lines, the smaller being on the latter locus. Thus, examination for the rarefaction shock possibility can be made at the saturated vapor locus, with the assurance that if the necessary condition be met anywhere in coexistence, it must also be met on this locus. We recall from Section IV that the most likely neighborhood for the occurrence of this condition in the single phase was also adjacent to the saturated vapor line, i.e., for  $V \approx (4/3) V_c$  and  $T = T(\min)$ .

By Eq. (15), the sign of  $\left( \frac{\partial^2 P_A}{\partial V^2} \right)_s$  is seen to be that of  $L(V, T)$ ; setting  $V = V_1(T)$  in Eq. (16) gives  $L(V_1, T)$  on the saturated vapor locus. Defining  $Z(T) = 1 + 3J/P_A'$ , and arranging the terms to show explicitly the dependence on the specific heat of the single phase, one obtains

$$L(V_1, T) = ZC_v^0 - T(C_v^0)' + K(T), \quad (22)$$

with

$$K(T) = ZM(T) - TN(T), \quad (23)$$

$$M(T) = C_{vA}(V_1, T) - C_v^0 = A + \{V_1 - V_3\} J(T), \quad (24)$$

and

$$N(T) = \left[ \frac{\partial (C_{VA} - C_V^0)}{\partial T} \right]_V (V_1, T) = A' - J V_3' + (V_1 - V_3) J' \quad (25)$$

All the terms making up the function  $K$ ,  $M$ , and  $N$  are explicit functions of  $T$ , independent of  $C_V^0$ , and can be computed numerically from Eq. (7). The numerical methods are satisfactory, except when  $T$  approaches  $T_c$ ; but here the limits of the functions can be found from a series expansion around  $T_c$ <sup>8</sup>. The computations are conveniently made in terms of the reduced variables formed by scaling  $P$ ,  $V$ , and  $T$  by their critical values.

The limits at  $T_c$  of most of the functions making up  $Z(T)$  and  $K(T)$  are given in Ref. [8]; the few others needed are shown in our appendix. The forms of  $Z(T)$  and  $K(T)/R$  are displayed in Figs. 1 and 2; they are both always positive, monotone decreasing with  $T$ , and have their smallest values of 8.200 and 31.86  $R$ , respectively, at  $T = T_c$ . With  $Z$  and  $K$  always positive in coexistence, Eq. (22) shows that if  $C_V^0$  is constant with respect to  $T$ ,  $\{(C_V^0)'\} = 0$ , there is no chance of a rarefaction shock in the two-phase region. This fact contrasts with the thermodynamic behavior of this fluid in the adjacent vapor phase, where a constant but large value of  $C_V^0$  permits  $\left(\frac{\partial^2 P}{\partial V^2}\right)_s$  to be negative. The only possibility of negative  $L(V, T)$  rests with  $T(C_V^0)'$  being larger than  $ZC_V^0 + K(T)$ , or in the form of an inequality,

$$T(C_V^0/R)' \geq [K(T)/R] + Z(T) (C_V^0/R) \geq 8.2 (C_V^0/R) + 31.86 . \quad (26)$$

#### D. Coexistence Boundary

For completeness, the change of  $\left(\frac{\partial P}{\partial V}\right)_s$  across the coexistence boundary should be investigated. Thus, a comparison of  $\left(\frac{\partial P_H}{\partial V}\right)_s$  for the single phase isentrope with  $\left(\frac{\partial P_A}{\partial V}\right)_s$  of coexistence, each evaluated at the same boundary point is needed to show the sign of any discontinuity

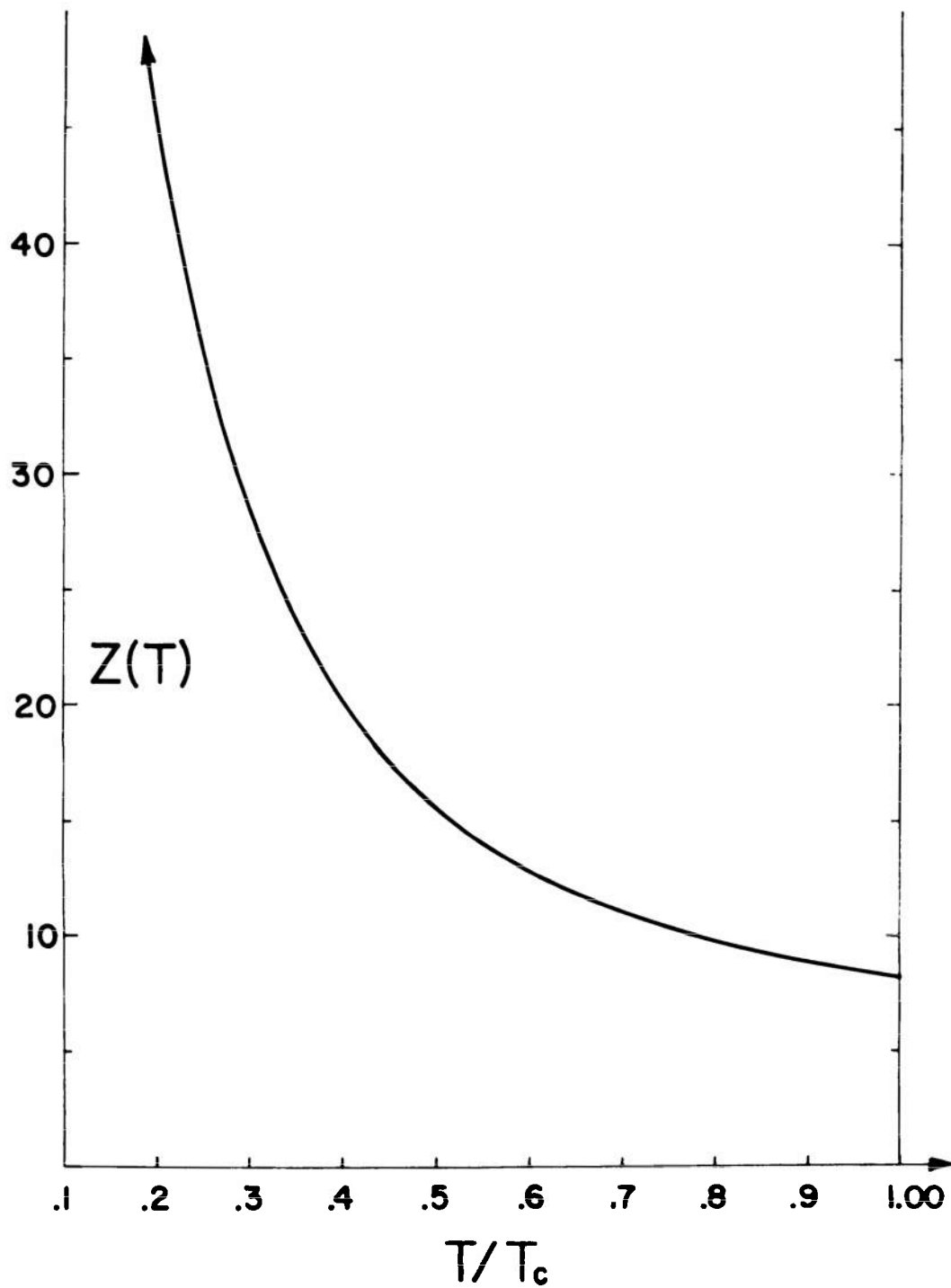


Figure 1. The dimensionless function  $Z(T) = 1 + 3T \frac{d^2 P_A}{dT^2} / \frac{dP_A}{dT}$  vs  $T/T_c$ .

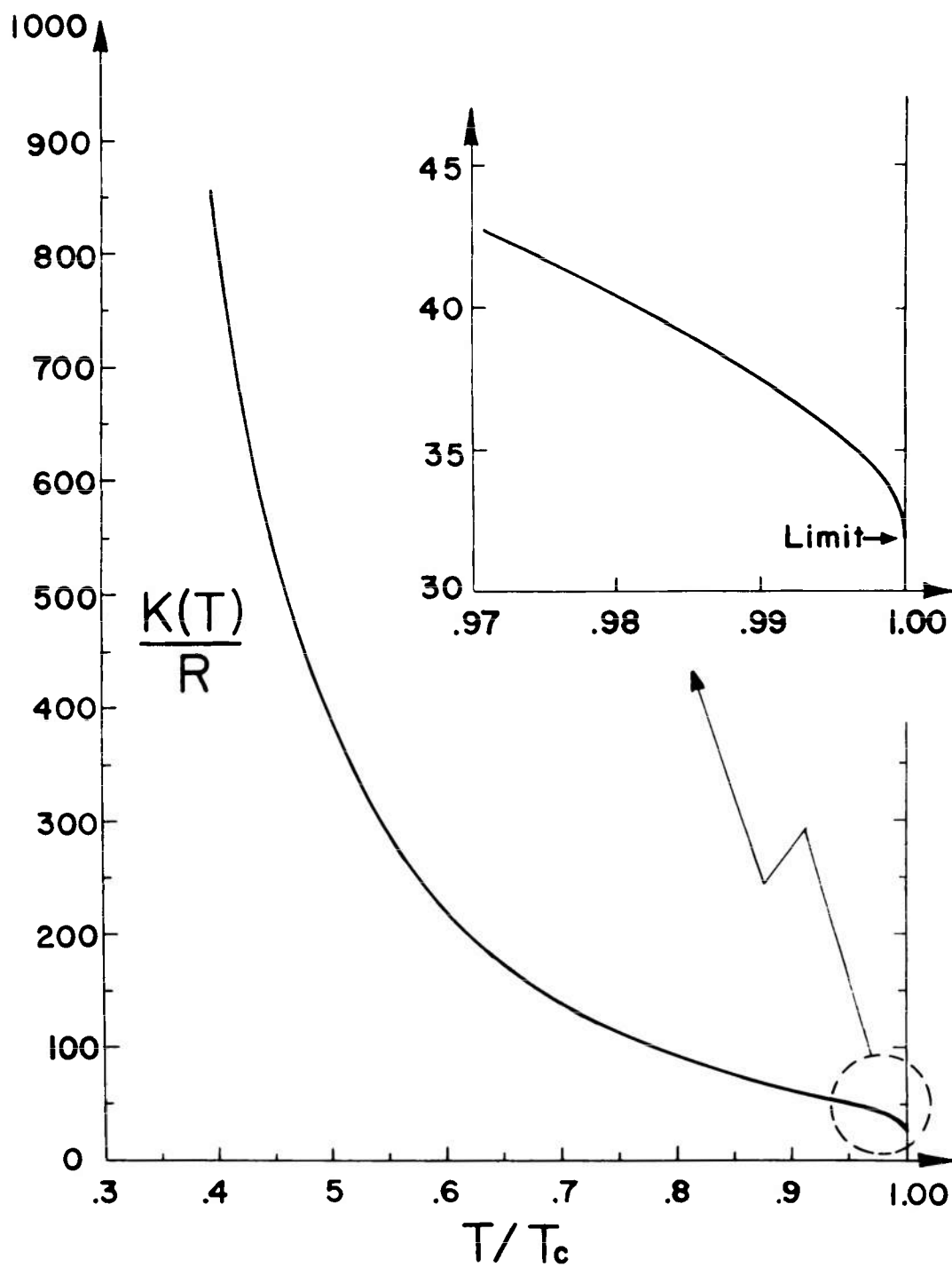


Figure 2. The dimensionless function  $K(T)/R$  {See Eqs. (23-25)} vs  $T/T_c$ .

in  $\left(\frac{\partial P}{\partial V}\right)_s$  across this boundary. This problem on the phase boundary for the liquid-vapor transition has previously been treated in Ref. [4], for an arbitrary equation of state; the discontinuity was always found to be positive. The Van der Waals-Maxwell fluid is no exception to this rule. We recall from Section II that  $\left(\frac{\partial P}{\partial V}\right)_s$  is everywhere negative for this fluid. Omitting considerable algebra we exhibit the result for  $\Delta = \left(\frac{\partial P_A}{\partial V}\right)_s - \left(\frac{\partial P_B}{\partial V}\right)_s$ , where all quantities are evaluated at a point on the phase boundary, either saturated liquid or vapor; the product of  $\Delta$  and  $C_{VA}(V_J, T)$  is

$$\Delta C_{VA}(V_J, T) = - (1/C_V^0) \left(\frac{\partial P_B}{\partial V}\right)_T \left\{ C_V^0 + TV_3 \left(\frac{\partial P_B}{\partial T}\right)_V \right\}^2 - f_J \left(\frac{\partial P_B}{\partial V}\right)_s, \quad (27)$$

with

$$f_J = TP_A'' \{V_J(T) - V_3(T)\} \quad (28)$$

and subscript  $J$  taking the value 1 or 3, depending on whether the boundary point lies on the saturated vapor or liquid locus, respectively. The quantity  $f_J$  is either positive or zero, while  $\left(\frac{\partial P_B}{\partial V}\right)_s$  is always negative, so the contribution from the second term of Eq. (27) is either positive or zero because of its negative sign. Meanwhile  $\left(\frac{\partial P_B}{\partial V}\right)_T$  is never positive on and outside the coexistence boundary, while  $C_{VA}$  is always positive, so  $\Delta$  is never negative. Hence, no rarefaction discontinuity can occur because of a negative jump in  $\left(\frac{\partial P}{\partial V}\right)_s$  across the coexistence boundary.

## VI. SPECIFIC HEAT FUNCTION

For this fluid, a necessary condition for the rarefaction shock depends explicitly on the constant volume specific heat. We explore briefly the expected contribution from a representative specific heat

function. Choosing the same units for  $C_V^0$  and  $R$ , the ratio  $C_V^0/R$  is dimensionless. To good approximation,  $C_V^0/R$  can be expressed in terms of translational, rotational and vibrational energy contributions, respectively, as<sup>14</sup>,

$$(C_V^0/R) = (C_V^0/R)(\text{tr.}) + (C_V^0/R)(\text{rot.}) + (C_V^0/R)(\text{vib.}). \quad (29)$$

We assume

$$(C_V^0/R)(\text{vib.}) = \sum_i g_i(x_i), \quad (30)$$

where all sums range from 1 to  $A$ , where  $A$  is the number of vibrational modes, and  $g_i(x_i)$  is an Einstein function given by

$$g_i(x_i) = (x_i / \sinh x_i)^2, \quad (31)$$

with  $x_i = \theta_i/(2T)$ , and  $\theta_i$  a constant for the  $i^{\text{th}}$  mode. Eq. (30) is usually applied to a polyatomic gas, where the first two terms on the right sum to a constant value  $B/2$  ranging between  $3/2$  and  $3$ , according to the molecular structure, and  $A = 3N - B$  where  $N$  is the number of atoms per molecule. If  $N > 2$ ,  $B$  is always  $6$ , a condition we henceforth assume. If optical modes (electronic vibration) are also included,  $A$  becomes correspondingly larger, as  $N$  must now include the electrons; however, the  $\theta_i$  for the optical modes are usually so high that they add little to the specific heat at temperatures less than  $5000^\circ \text{K}$ <sup>14</sup>.

From the forms of Eqs. (29) and (30), it follows that

$$T(C_V^0/R)' = \sum_i^A k_i(x_i) \quad (32)$$

with

$$k_i(x_i) = 2 x_i^2 [x_i \cosh x_i - \sinh x_i] / (\sinh x_i)^3. \quad (33)$$

This function  $k_1(x_1)$  has a maximum value of .6757 at  $x_1 = 1.744$ ; while  $g_1(x_1)$  has its largest value of 1 at  $x_1 = 0$ . Therefore,

$$T(C_v^0/R)' \leq .676 A, \quad (34)$$

where equality is approached only if all  $\theta_1$  have the same value, and  $k_1$  is at its maximum; and

$$\sum_1^A g_1(x_1) \leq A, \quad (35)$$

where the equality is approached only if every  $\theta_1 \ll T$ , so each  $x_1$  is nearly zero. With the assumption  $B = 6$ , use of Eqs. (29) and (35) gives

$$3 \leq C_v^0/R \leq 3 + A. \quad (36)$$

## VII. RAREFACTION SHOCK POSSIBILITY

With the preceding model for the specific heat, one may now assess the chance of satisfying the necessary condition  $\left(\frac{\partial^2 P}{\partial v^2}\right)_s < 0$  for the rarefaction shock in this fluid.

### A. Ideal Gas

One seeks conditions where  $\phi(T)$  might be negative. Making use of the strongest form of the inequalities Eqs. (34)-(36) in the definition of  $\phi(T)$ , yields the very strong inequality

$$\phi(T) > 2 - .676 A/27. \quad (37)$$

One concludes that  $\phi$  could not possibly be negative for  $A$  less than 80 modes; this condition appears to exceed reality sufficiently as to be practically impossible. Actually, a weaker form of inequality indicates

A must be very much larger, as pointed out in Ref. [4]. For example, assuming all  $\theta_i = \theta_1$ , then

$$\phi(T) > 2 - W(A, x_1) = 2 - Ak_1(x_1)/[3 + Ag_1(x_1)]^3. \quad (38)$$

$W(A, x_1)$  has a single maximum with respect to A, denoted by  $W_m(x_1)$  at  $A = 3/[2 g_1(x_1)]$ .  $W_m(x_1) = (4/243)(f_1/g_1)$ , where  $(f_1/g_1) = 2(x_1 \cosh x_1 - \sinh x_1)/\sinh x_1$ , and  $W_m$  increases monotonically with  $x_1$  from its zero minimum value with respect to  $x_1$ , occurring at  $x_1 = 0$ . For large  $x_1$ ,  $(f_1/g_1) \approx 2(x_1 - 1)$ , and  $W_m(x_1) \approx (8/243)x_1$ ; this latter quantity approaches the value 2 for  $x_1 \approx 61$ , so that  $A \approx 10^{49}$ . Thus, the rarefaction shock possibility in the ideal gas is effectively ruled out.

#### B. Single Phase, Van der Waals

Here the test is to see if Eq. (11) can be fulfilled. Computations show the largest value of  $G(V, T)$  to be 2.184 at  $V/V_c = 1.483$ , and  $T/T_c = .9711$  (a point on the saturated vapor line). Here  $C_v^0/R \geq 16.65$  will satisfy Eq. (11), independent of  $(C_v^0/R)'$ ; attaining this condition requires at least  $A = 14$  modes, each one almost completely excited at a temperature near critical for the substance.

#### C. Equilibrium Coexisting Phases

For this domain, one searches for conditions which might satisfy inequality Eq. (26). Again making use of Eqs. (34) and (36), one finds that Eq. (26) cannot be fulfilled for A less than 83 vibrational modes, each of whose  $\theta \approx 3.5 T_c$  for the substance. This restriction for practical purposes nullifies the rarefaction shock probability in the equilibrium coexistence state of this fluid.

### VIII. COMPARISON WITH STEAM TABLES

Following the appearance of the early analysis by Zeldovich for the vapor phase of the Van der Waals fluid, a short treatment by

Novikov<sup>9</sup> was given for the two-phase state of steam. By using an adiabatic differential equation of state and the resulting interpolating formula with (unreferenced) steam tables, Novikov concluded that the necessary condition for the rarefaction shock could be satisfied in the two phase region near critical. For comparison, we show several equilibrium isentropes for steam in this region, using given tables<sup>15</sup>. This is done by noting that the entropy is linear in  $V$  on the isobaric isotherm segment in coexistence; or, for fixed  $T$  and  $P$ ,

$$S(V,T) = S(\text{sat. liq.}) + \Delta S \{V - V(\text{sat. liq.})\} / \{V(\text{sat. liq.}) - V(\text{sat. liq.})\},$$

where  $\Delta S$  is the vaporization entropy for this  $T$ . Thus, one can find from the tables a value of  $V$  for fixed  $S$  and various  $T$  (or  $P$ ). Numerical differentiation of the resulting equilibrium isentropes then shows where  $\left(\frac{\partial^2 P}{\partial V^2}\right)_S \leq 0$  in coexistence. We confirm Novikov's conclusion for a region between  $P/P_c \approx .92$  and  $1.00$ . Fig. 3 shows an enlarged view of the coexistence boundaries for both steam and the theoretical Van der Waals-Maxwell fluid, as well as representative isentropes for each. The steam region where  $\left(\frac{\partial^2 P}{\partial V^2}\right)_S < 0$  is enclosed by its saturation locus and the nebulous hatched boundary indicated at  $P/P_c \approx .94$ . This diffuse lower boundary could not be more precisely defined because of the lack of significant figures in the steam table data. All but one of the isentropes for the theoretical model correspond to  $C_v^0/R = 3/2$ . Two theoretical isentropes passing through the critical point were computed, one for  $C_v^0/R = 3/2$  and one for  $C_v^0/R = 5/2$ ; this latter one has only a slightly larger slope than the former.

Fig. 3 also illustrates a common fault of the Van der Waals-Maxwell model in the critical region: its scaled saturation locus is much less flat at critical, and lies well inside that for steam; the same behavior is noted with respect to many other substances<sup>16</sup>. Although the particular steam tables used here indicate the necessary condition for the rarefaction shock is met in a small coexistence region

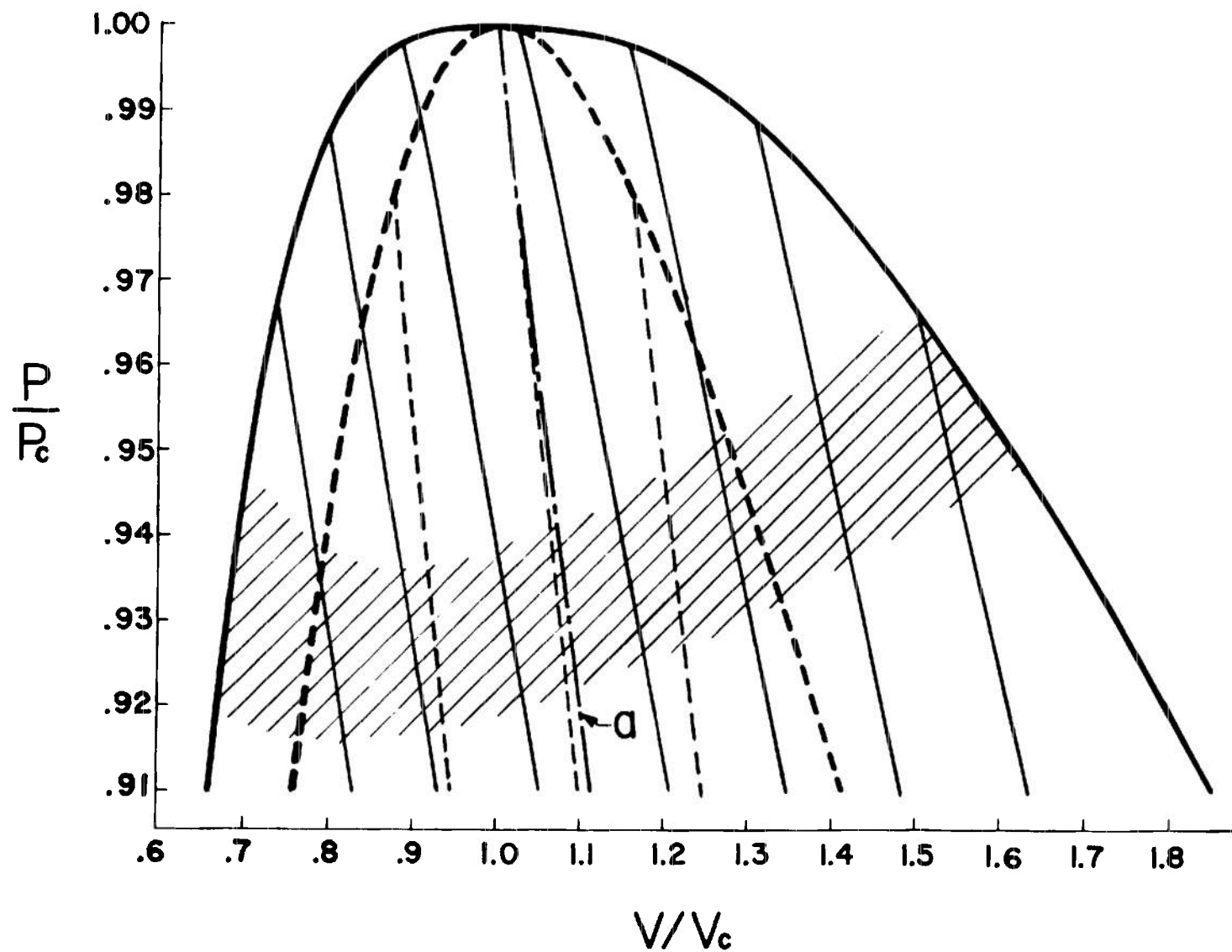


Figure 3. Scaled coexistence boundaries and isentropes near critical for steam (solid curves) and the Van der Waals fluid (dashed lines). For steam  $\left(\frac{\partial^2 P}{\partial V^2}\right)_s < 0$  in the enclosed region above the hatching.

near critical, it is by no means certain that such a discontinuity would actually develop. The critical temperature for steam is quite low  $\{T_c \text{ (steam)} = 647^\circ \text{ K}\}$  and there is a good possibility that metastable supersaturation of the liquid phase would occur during adiabatic expansion. Such a metastable state is less likely at much higher temperatures. One might then conjecture that if correspondence holds between steam and a fluid with a much higher critical temperature, the latter substance might support a rarefaction discontinuity.

## IX. SUMMARY

This investigation for the rarefaction shock condition in an equilibrium Van der Waals-Maxwell fluid has shown it to be practically impossible in and across all phase regions. Comparison with steam tables, however, shows that a necessary condition for the discontinuity does exist in principle, in the equilibrium coexistence state near critical. The Van der Waals fluid model used here is recognized as not accurately describing a real fluid in the critical region. Here it might prove useful to perform a similar investigation using more modern concepts about critical state behavior<sup>18</sup>. However, despite promising progress, these modern approaches of the critical region do not yet appear to have produced a sufficiently simple and differentiable state equation as to enable completion of such an investigation.

Although the rarefaction discontinuity was shown to be impossible across a liquid-vapor transition boundary<sup>4</sup>, some solid-solid and liquid-solid phase transitions do contain the necessary conditions for this discontinuity. These are mentioned in Refs. [4] and [17], with some experimental evidence for their existence offered in Ref. [19].

## X. ACKNOWLEDGEMENTS

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## APPENDIX

The limiting values of many quantities making up the  $L(V_1, T)$  defined in Eq. (22) for the coexistence state are tabulated by Barieau<sup>8</sup>. His method employed a power series expansion of reduced density along the saturated boundary near critical. The reduced variables were  $\beta = P/P_c$ ,  $\gamma = T/T_c$  and  $\alpha = V_c/V$ , and  $\alpha_j$  with  $j = 1$  or  $3$  representing reduced densities on the saturated vapor and liquid loci, respectively. All other thermodynamic quantities for the coexistence state can be expressed in terms of these  $\alpha_j$  and their scaled temperature derivatives. The Maxwell rule gives a functional relationship between  $\alpha_1$  and  $\alpha_3$ ; defining  $y = \alpha_3 - 1$  and  $x = 1 - \alpha_1$ , the power series expansion using the Maxwell rule is

$$y = \sum_{i=1} a_i x^i. \quad (A1)$$

Barieau found the first three coefficients to be  $a_1 = 1$ ,  $a_2 = (1/5)$  and  $a_3 = (1/25)$ . In order to find the limit at critical of our functions  $B'(T)$ ,  $N(T)$ , and  $K(T)$  it was necessary to find the fourth order coefficient, which we determine to be  $a_4 = (19/350)$ . It is understood that within coexistence the pressure,  $P$ , is the vapor pressure  $P_A$ . We further adopt the notation that a prime on a reduced variable denotes differentiation by reduced temperature,  $\gamma$ . Then our dimensionless function  $Z(T) = 1 + 3\gamma\beta''/\beta'$  has the limiting value at critical of 8.2. Making use of  $a_4$ , we further find that the critical limit of  $\beta'''$  is 5.5954. The function  $J'(T)$  is equal to  $(P_c/T_c^2)\{\gamma\beta''' + \beta''\}$ , and has the limiting value at critical 15.1954  $(P_c/T_c^2)$ . We show in Fig. 4 the the behavior of  $J'(T)(T_c^2/P_c)$ , always positive in the range of interest.

The form of  $N(T)$  given by Eq. (25) does not permit finding its limit simply by taking the sum of the limits of each term on the right, because these term limits are  $+\infty$  and  $-\infty$ ; instead, a tedious expansion of this sum of terms using Eq. (A1) yields at critical the limiting value of

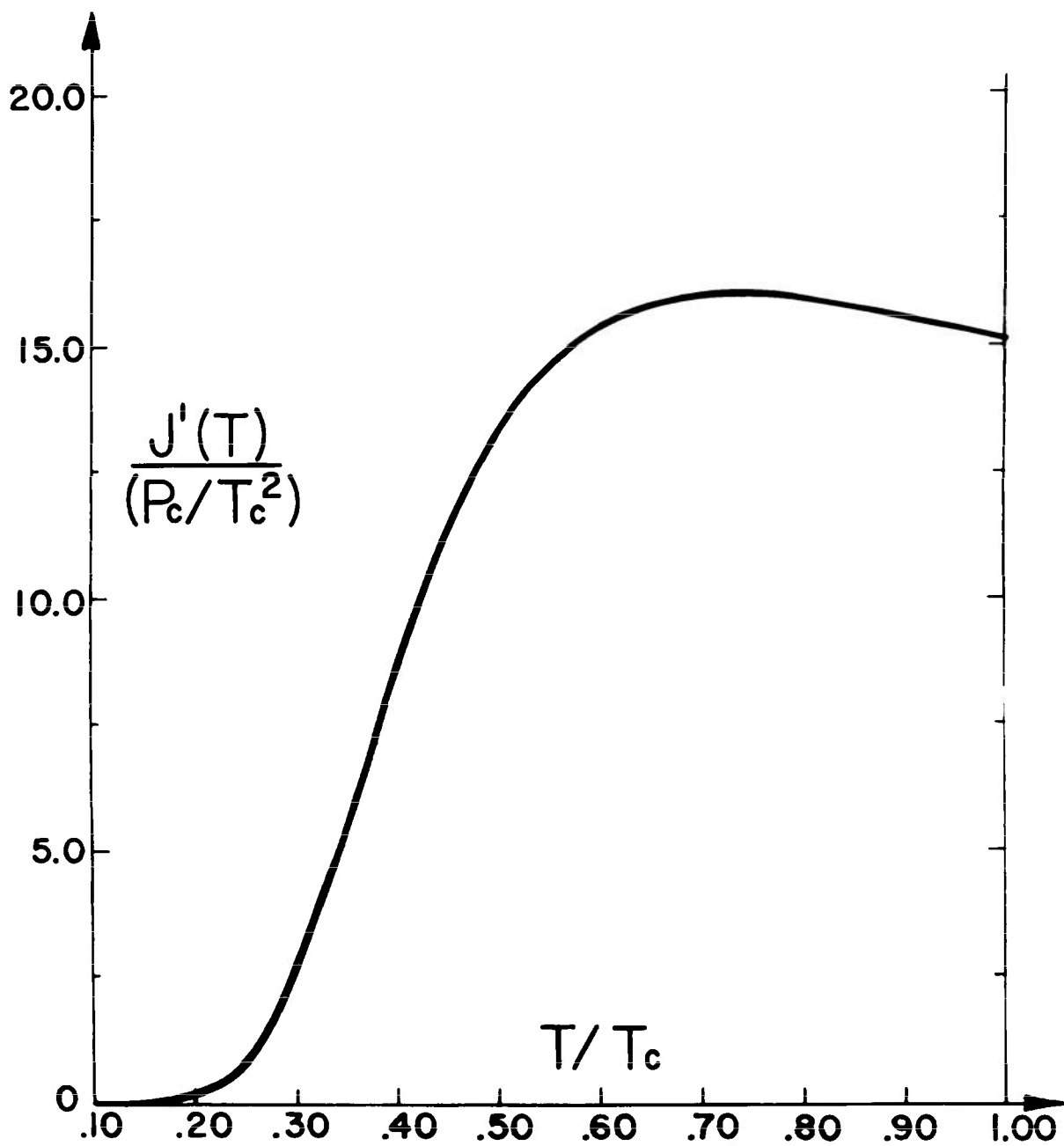


Figure 4. The scaled function  $(T_c^2/P_c) J'(T)$  vs  $T/T_c$ .

$$\text{Lim } \{N(T)\} = (3/8)(R/T_c)(13.4440)$$

and  $\text{Lim } \{TN(T)\} = (3/8)R(13.4440)$ . Moreover, since  $\text{Lim } \{M(T)\} = 4.5R$ , then  $\text{Lim } \{K(T)/R\} = 31.860$ .

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13. ABSTRACT  The rarefaction shock is found to be impossible practically in an equilibrium Van der Waals-Maxwell fluid, in and across all phase regions. The existence of this type shock depends explicitly on the constant-volume heat, as well as the pressure equation of state. The form of specific heat assumed here includes contributions from translation, rotation, and vibration energies of the molecule; Einstein functions are used to represent the latter. In particular, the vaporizing expansion wave in the saturated liquid phase cannot be discontinuous. Metastable states of supersaturation are not considered. Despite the results for this theoretical model, the necessary conditions for the rarefaction shock are found to be satisfied, in principle, for a small region near the critical point of a real two-phase fluid (steam).			

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